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Time Dependent Effects of External Fire on Chemical Reactive Hazards

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Abstract

An external fire can often be the defining case when sizing a relief device for chemical reactive hazards. Batch reaction systems can have multiple reactions or have reactions with multiple steps. Analyzing every possibility is impractical, so relief device sizing is often performed by conducting only one test or simulation per scenario. However, this simplification can obscure potentially significant effects which might then be overlooked in the analysis. For example, a fire that is started while the main reaction is underway could result in an overpressure (due to an exotherm or decomposition reaction) less severe than one that starts once the final product has completely formed. This can be due to reactants for the main reaction being boiled off before the conditions for the worse case are reached. Other factors that should likewise be considered when performing transient analysis for external fire on reactive systems will be further discussed within the paper.

Introduction and Background

In the chemical processing industry, poor or improper design of the emergency pressure relief system for reactive hazards may cause a rupture of the containment vessel, leading to possible fires, explosions, or toxic exposure to personnel or the public, depending on the chemicals present. A 2002 United States Chemical Safety Board (US CSB) study on reactive hazards identified "167 serious accidents involving uncontrolled chemical reactions that occurred between 1980 and 2001". The result of these accidents was "a total of 108 deaths and hundreds of millions of dollars in property damage".[1]

An accident at T2 Laboratories in Jacksonville, Florida in 2007 was determined to be due to a runaway chemical reaction in a 2500-gallon batch reactor causing 4 fatalities and 32 injuries. Following the incident, the US CSB released a report advising companies to "identify and thoroughly evaluate reactive hazards in their processes, implement appropriate emergency pressure relief systems and other design standards… and carefully manage any changes to existing processes…"[2]

Two common reactive hazards resulting in overpressure are runaway exothermic reactions and thermal decomposition or gas producing reactions. A runaway exotherm feeds itself and results in an exponential increase in temperature until a reactant depletes. A thermal decomposition reaction, though often endothermic, involves the breakdown of larger molecules into numerous smaller molecules that are gaseous or more volatile. Depending on the chemistry, either or both of these reactions may lead to rapid pressurization of the containment vessel. The rate of reaction and subsequent pressurization further escalate with increased temperature.

Among the potential causes of the temperature excursion leading to either a runaway exotherm or thermal decomposition are (per API Std 521 Section 4.4.11):[3]

- external fire
- loss of mixing
- loss of cooling
- incorrect charge of reagents

Each of these potential overpressure scenarios requires careful evaluation and knowledge of the reactive process and the tools and methodologies for evaluating the relief system design. RAGAGEP for the reactive hazard evaluation and pressure relief system design includes the DIERS Project Manual[4], CCPS "Guidelines for Pressure Relief and Effluent Handling Systems,"[5] and API Std 521[3]. The general procedure is to first perform a bench scale test to simulate the upset condition, and then to use the results of the test to characterize the system. Once the reaction is characterized, the relief case can be modeled to determine the overpressure protection requirements. Depending on the overpressure scenario under consideration, the relief case model configuration may change, in terms of heat added/removed (fire/loss of cooling/mixing), feed added (incorrect charge), and homogenous concentration assumptions (loss of mixing). When evaluating the relief case in a transient model, the modeling assumptions for the external fire heat input should be carefully considered, as the impact on the relief system design can be significant.

Bench Scale Test and Reaction Modeling

Identification of reactive hazards at temperatures above that of the intended main reaction can be performed by conducting a calorimetry test. The purpose of the calorimetry test is to determine at what temperatures different chemical reactions occur, as well as estimate their rate and exothermicity.

The test is typically performed by mixing the components per the normal reaction procedure; then, upon reaching a stable temperature, adding heat slowly and periodically, until a set limit has been reached. Typical readings include pressure and temperature data as the system temperature is increased. For liquid phase reactions, the pressure rise is typically due to vaporization of the reactor contents or a reaction producing moles of gas. Note that there are often multiple reactions that can take place in a single calorimetry test, and each reaction will have its own rate equation and rate constant. Gas sample analysis and liquid composition analysis can also be conducted to identify the abnormal reaction products and help characterize the reactions.

Once the reactions in the bench scale test have been characterized, the collected temperature and pressure data can be reproduced in a model, where the kinetics and activation energy for each reaction can be tuned to reproduce the observed results. The adiabaticity (phi factor) of the calorimeter should also be identified and considered in the determination of the heat of reaction. It should be noted that each calorimetry technique has its own set of limitations and should be carefully weighed when analyzing reactive hazards. For example, the bench scale test containment vessel temperature and pressure rating is a practical limit on the data collection; any reactive behavior that occurs at temperatures above the test pressure may require further analysis to identify.

Pressure Relief Modeling for the Reactive System

API Std 521 states that, "[w]here feasible, a pressure relief device should be used to control overpressure."[3] To determine the sizing of the pressure relief device, a transient model of the reactive system, including the vaporization of material in the reactive system due to heat input from external fire, and the analysis of onset and disengagement of 2-phase relief, can be performed using a simulation package and following the methodologies outlined in API Stds 521 & 520 Part I and in the CCPS and DIERS literature.[3][4][5][6]

- Modeling of the external fire heat input to the pressure containing system can be done using the API Std 521 empirical equation or the analytical method described in Annex A, with allowable credits for insulation or other heat input reduction factors.
- The capacity of the pressure relief device can determined using the direct integration sizing equation described in API Std 520 Part I Annex B, as two phase relief is often expected.
- The two-phase onset and disengagement behavior (including calculation of the liquid swelled level height at any point in time) can be modeled using the guidance in the DIERS Project Manual or other DIERS literature.

When modeling the reaction behavior during the upset conditions, there are two important temperature-dependent considerations affecting the reaction rate: the reaction rate constant and volatility. The reaction rate constant (as defined by the Arrhenius equation) is dependent on the activation energy and the temperature.

$$k = k_0 e^{\frac{-E_a}{RT}}$$

With more energy in the system due to the external fire heat input, the rate of each reaction is expected to increase. This also changes the concentration of each component in the system as the intended reaction is replaced by unintended side reactions. Volatility affects the reaction rate in the opposite manner; for liquid phase reactions, vaporization of a component removes moles from the liquid concentration, and, depending on the order of the reaction, this can drive the reaction rate down, and ultimately terminate a reaction. It is also important to recognize that the volatility of any system component can reduce the overall composition of the reactor system contents; as the system is modeled with two phase relief, the venting of vapor can carry liquid components out through the relief path.

In a steady state model, as long as flammable sources are in the area, an external fire is often taken as a given and the fire heat input assumed constant. Because the model of the relief rate is constant, the question of when the fire starts and stops is somewhat irrelevant, and therefore often ignored. However, if the same assumptions are carried over to a transient model, starting the fire simultaneously with the start of the reaction process, the results may be misleading. For example, the fire may interfere with the loading of the reactor, the duration of fire exposure could boil off reactants before an exotherm is reached, or the heat from the fire could push the temperature beyond a self-heating limit such that the reactor may not see an exotherm until well after the fire is extinguished.

Rather than suggesting a fully dynamic model of the fire heat input, which would add a significant amount of complexity and permutation to an already complex and computationally intensive process, it is proposed that the heat input due to external fire can be modeled with the simplified assumption of constant heat input, but with consideration given to the fire initiation time, fire duration time, and post-fire time.

Note: the thermal mass of the reactor contents (mC_p) is an important factor in any transient model of external fire, affecting how quickly the temperature of the contents will rise due to heat input (the time required to reach the bubble point or reaction onset temperature is often referred to as the heat-up time); however, it is a constant consideration and not specific to any particular time domain.

Fire Initiation Time

The following should be considered when determining the most appropriate point in time to model the fire heat input.

Reaction operation procedure – How would a fire impact the charging of the reactor?

The first consideration is the reactor charging procedure. If the reactor charge is automatic, then charge to the reactor may continue uninterrupted. However, if the charge is manual, there may be a period where it is unlikely the reactor feed procedure would continue normally. For example, in one instance evaluated, the reactor charge was fed by a hopper which required the operator to open multiple sacks of reactor feed (transported via forklift). If the fire broke out after the first sack of reagent was added, it was determined the operator would not re-enter the area to continue adding more reagent.

Additionally, if the reactor feed is controlled by automated safety systems, the response of the safety systems due to pressure or temperature deviations resulting from the fire heat input may impact the model (depending on the reliability of these systems, with special consideration of their reliability in the event of fire).

<u>Component concentration</u> – What components will be present when the fire starts?

Depending on the reaction equation and order for each reaction, the reaction rate(s) may be driven by the concentration of specific components. Prior to the start of the fire, the intended reaction(s) can be expected to proceed normally. If these result in the production of more stable, less volatile components, then this can slow the pressurization rate of the system, and vice versa. Similarly, decomposition of the reagents may be more or less severe than decomposition of the products. However, due to the all the potential factors involved, this can be a difficult thing to predict, and may require trial and error to identify the worst case.

Fire Duration Time

After the fire has started and heat is being modeled as an active input to the reactive system, the following should be considered when determining the duration of the fire.

<u>Length of fire exposure</u> – How long is the pressure containing system exposed to the external fire?

Both NFPA 30 and API Std 521 require that the installation (or components thereof) be designed to withstand a minimum of two hours of fire exposure (given in terms of temperature exposure). Beyond the two hours, the integrity of the equipment, insulation, or the supporting structure may be compromised. Even if there is no loss of containment, the effective maximum working pressure may be reduced to the point where the protection of the equipment can no longer be provided by a pressure relief device (i.e., the set pressure of the pressure relief device is above the effective MAWP), and other forms of protection or risk mitigation may be required. For this reason, transient fire pressure relief models (including non-reactive models) are often run with a limit of two hours.

However, for reactive systems, it is a better practice to also consider the pressure relief device response. If the pressure relief device has opened prior to the close of the two-hour window, then, if the relief device is still open or close to opening, then letting the fire heat input continue may produce a worse case result for the pressure relief system design. If the pressure relief device has not lifted, but will open shortly after the two-hour window, then the pressure relief system design should consider the sizing based on this case. For example, in one model, it was determined that relief would occur at 2 hours and 14 minutes after the start of the fire; the pressure relief system was sized for the fire relief load and documented as such. However, care should be exercised that the duration of fire exposure does not exceed common sense. Note that regardless of the fire duration modeled, if credit was taken for reduced heat input due to fireproof insulation, this credit should not be taken after two hours of fire exposure.

If the pressure relief device has already opened, vented, and reclosed, and the pressure rise rate is not likely to reopen the device (i.e. the overwhelming majority of the reactor contents have been vented off already), then continued fire heat input is not likely to increase the required size of the pressure relief device; rather, loss of the liquid contents to absorb the fire heat would likely result in overtemperature of the vessel walls. An interesting side note is that increasing the size of the pressure relief device can also contribute to this result, in that the larger area expedites the venting off of the reactor contents.

There is also the possibility that a longer duration of fire exposure can make the relief requirement less severe. In one example, two hours' worth of fire exposure managed to vent off the contents of the reactor to the point that the exotherm was not the determining factor in the relief system design. If the fire had lasted a shorter duration, it is theoretically possible that a worse case relief requirement might emerge due to having more reactants in the liquid phase to produce the exotherm or to thermally decompose. This potential should also be considered if and when choosing to extend the fire beyond the two-hour window (i.e., letting the model run longer with fire heat input can boil off the components that may have led to a secondary exotherm). While it may not be practical to check for this possibility at every possible fire duration, simply being aware of the basis for the pressure relief system design (fire vaporization vs. exotherm) can help determine the most appropriate response.

Post-Fire Time

Length of time after fire is extinguished – After the fire is extinguished, is there still a risk of overpressure due to a runaway exotherm?

In the event that the transient model does terminate the fire heat input after 2 hours of exposure, it is important not to simply stop the analysis there. Having absorbed the heat from the fire, the reactive system may still have received enough energy to start a self-heating reaction, starting down the path to a runaway exotherm. It is possible that this relief may not be observed until many hours later.

Conclusion

The US Chemical Safety Board, the American Petroleum Institute, and the Design Institute for Emergency Relief Systems have all stated the importance of considering the impact of external fire on the pressure relief system design for reactive systems. Although powerful tools and methodologies are available to perform detailed transient analysis of overpressure scenarios for reactive systems, when getting down to the details of modeling these scenarios, it is important not to overlook the impact of our assumptions. For the external fire overpressure scenario specifically, we can gain a better understanding of the potential problems by asking a few simple questions:

- How is the reaction going to proceed when the fire starts?

- What will be present in the reactor when the fire starts?
- For how long should the fire be modeled?
- What should be done after the fire heat input stops?

No company has an unlimited budget to run an infinite number of model permutations; however, awareness of the impacts of time-dependent factors lets the user exercise discretion and determine the most appropriate modeling assumptions.

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